

# Lanthanoids

(1)

Elements: La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu

They are also called lanthanides, R.E.E (rare earth elements).

## Electronic configuration

Element	atomic no.	Full name	electronic configuration
La	57	Lanthanum	$[Xe] 4f^0 \underline{5d^1} 6s^2$
Ce	58	Cerium	$[Xe] 4f^1 \underline{5d^1} 6s^2$
Pr	59	Praseodymium	$[Xe] 4f^3 6s^2$
Nd	60	Neodymium	$[Xe] 4f^4 6s^2$
Pm	61	Promethium	$[Xe] 4f^5 6s^2$
Sm	62	Samarium	$[Xe] 4f^6 6s^2$
Eu	63	Europium	$[Xe] 4f^7 6s^2$
Gd	64	Gadolinium	$[Xe] 4f^7 \underline{5d^1} 6s^2$
Tb	65	Terbium	$[Xe] 4f^9 6s^2$
Dy	66	Dysprosium	$[Xe] 4f^{10} 6s^2$
Ho	67	Holmium	$[Xe] 4f^{11} 6s^2$
Er	68	Erbium	$[Xe] 4f^{12} 6s^2$
Tm	69	Thulium	$[Xe] 4f^{13} 6s^2$
Yb	70	Ytterbium	$[Xe] 4f^{14} 6s^2$
Lu	71	Lutetium	$[Xe] 4f^{14} \underline{5d^1} 6s^2$



The ground state electronic configuration of the lanthanide elements are generally of the type  $[Xe]4f^n 6s^2$ . Lanthanum is though outside this generalisation, it can be included in the list due to its properties like other lanthanides. (2)

exception in electronic configuration:  $4f^1 5d^1$  instead of  $4f^2 5d^0$  because the nuclear charge is insufficient to contract the  $4f$  orbitals and lower their energy below  $5d$ . So,  $5d$  and  $4f$  orbitals are of very comparable energies. Gadolinium also has  $f^7 d^1$  configuration instead of  $f^8$  configuration due to enhanced stability of the half-filled shell. Similar is the case for the last element of the R.E.E. i.e. Lu where configuration is  $f^{14} d^1$ .

Atomic and ionic radii:  $\rightarrow$  See lanthanide contraction as discussed earlier in the 'periodicity' chapter.

Oxidation States: The principal oxidation state for all these elements is  $+III$ . The elements adjacent to  $f^0$ ,  $f^7$  and  $f^{14}$  configuration may show other oxidation states due to stability of the empty, half-filled and full-filled subshell.

Ce  $\rightarrow$  IV, III, Pr  $\rightarrow$  IV, III, Yb  $\rightarrow$  II, Tm  $\rightarrow$  II  
 Eu  $\rightarrow$  II, Tb  $\rightarrow$  IV, Dy  $\rightarrow$  IV

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd
<u>3</u>	<u>3</u> , 4	<u>3</u> , (4)	<u>3</u>	<u>3</u>	<u>3</u> , (2)	<u>3</u> , (2)	<u>3</u>
Tb	Dy	Ho	Er	Tm	Yb	Lu	
<u>3</u> , (4)	<u>3</u> , (4)	<u>3</u>	<u>3</u>	<u>3</u> , (2)	<u>3</u> , (2)	<u>3</u>	

underlined  $\rightarrow$  most common oxidation state

parenthesis  $\rightarrow$  less " " "



The common occurrence of the +3 oxidation state for all lanthanides appears to be a consequence of greater stabilisation of 4f orbitals in comparison to 5d or 6s with increasing ionic charge. The order of penetration of the orbitals runs as:  $4f > 5d > 6s$ . As successive ionisation increases, the net charge on the lanthanide cation, the 4f electrons are thus stabilised to a greater extent. Hence, 5d and 6s electrons are ionised in most cases.

● If +II and +IV oxdn. state of Ln-ions are ascribed to stability of the half-filled and full-filled shell  $\rightarrow$  then why not  $\text{Sm}^+(f^7)$ ? or,  $\text{Tm}^+(f^{14})$ ?

Similarly, why not  $\text{Pr}^{5+}(f^0)$  or  $\text{Nd}^{+6}(f^0)$ ?

Hint: Formation and stabilisation of any ion in a particular oxdn. state may be depicted in a relevant Born-Haber cycle in terms of several enthalpy terms like ionisation pot./sublimation/ $U_L$  etc. Thus, the stabilised oxdn. state of any element is a consequence of several factors that play roles.

### ● Complex formation

In general, the lanthanide elements show much less tendency towards complex formation compared to d-block elements. Their larger size and lower electronegativity leads to increased ionic character in the bonds. The f-orbitals are somewhat inert in participation in bonding. But in some cases i.e. in complexes of high coordination no. or in the complexes with regular cuboid geometry, participation of f-orbitals are evident.

features: 1) Lanthanoids exhibit high C.N. with smaller ligands and C.N.  $< 6$  only when ligands are very bulky.

2) Prefers O-donor ligands (Hard-type).

3) They can easily change geometry, shape. Hence, complexes are labile.

4) Stereoisomerism is a common phenomenon.

5)  $\text{Ln}^{3+}$  ions are strongly hydrated, hence only strong chelating ligands can displace aquo-molecules. The complexes are seen to have water molecules as coordinating ligands. (aquo-complexes are common).



## Spectral and magnetic properties

(4)

### ① Colour of the ions

Colourless  $\rightarrow$   $\text{La}^{3+} (f^0)$ ,  $\text{Ce}^{3+} (f^1)$ ,  $\text{Gd}^{3+} (f^7)$ ,  $\text{Yb}^{3+} (f^{14})$   
 $\text{Lu}^{3+} (f^{14})$ .

Coloured  $\rightarrow$   $\text{Pr}^{3+}$ ,  $\text{Tm}^{3+} (f^2, f^{12}) \rightarrow$  green  
 $\text{Nd}^{3+}$ ,  $\text{Er}^{3+} (f^3, f^{11}) \rightarrow$  lilac  
~~Gd~~  $\text{Pm}^{3+}$ ,  $\text{Ho}^{3+} (f^4, f^{10}) \rightarrow$  pink, yellow  
 $\text{Sm}^{3+}$ ,  $\text{Dy}^{3+} (f^5, f^9) \rightarrow$  yellow  
 $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+} (f^6, f^8) \rightarrow$  pale pink

It is seen that, ions with configuration  $f^n$  and  $f^{14-n}$  configuration have similar colours. Colours are produced by absorption of electromagnetic radiation in the visible region corresponding to transition of the ions from their ground states to excited states. For the  $\text{Ln}^{3+}$  ions, such excited states arise from the same  $4f^n$  configuration as the ground term. The transitions involved are thus mainly  $f-f$  transitions, which are forbidden (like  $d-d$  transitions). Hence, the colours of the  $\text{Ln}^{3+} (\text{aq})$  ions are less intense.

● Question: Compare between  $d-d$  and  $f-f$  transitions.

Similar question: Explain; electronic spectrum of lanthanoid ions consist of typically a large no. of sharp bands.

Hint: 1) The  $f$ -orbitals lie deep in the atom and are shielded from interference by the nature of the ligands or by thermal vibrations. The bands arising from  $f-f$  transitions are thus sharp (compared to  $d-d$  transition, as  $d$ -orbitals are affected more by ligand fields).

2) Spin-orbit coupling for the lanthanides is more important than crystal-field effects. The states with different  $J$  values are widely apart and bands are sharp.

3) The no. of theoretically possible transitions are large, giving several peaks in the electronic spectrum. (for a high  $l$  value, several  $m_l$  values).



## magnetic properties

The trivalent rare earth ions have incompletely filled 4f - (5) subshell which is a source of their magnetism. Their 4f - subshell is quite deep seated and is shielded from the disturbing effects of surrounding ions (i.e. crystal field effect). They are thus, behave as, perfect ions. Furthermore, the J - levels are widely separated due to strong  $\vec{L} - \vec{S}$  coupling. They conform to the case of wide multiplet widths compared to  $KE$ , so that their magnetic moments are obtained by the eqn:  $\mu = g \beta \sqrt{J(J+1)}$

Where,  $g =$  gyromagnetic ratio

$$= 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

Thus, states with higher J - values (higher than g.s.) are usually unoccupied. This is reflected in the observed magnetic moments which are in good agreement with those calculated from J values but differ widely from the Spin-only values.

exception: i)  $\text{Sm (III)}$  (ii)  $\text{Eu (III)}$   $\rightarrow$  higher magnetic moment arises due to mixing of states at ordinary temp. and two or more excited states are populated.

Highest  $\mu$  for  $f^n$  ions  $\rightarrow \text{Dy (III)}$ ,  $\mu = 10.63 \text{ B.M.}$   
Lowest  $\mu$  for  $f^n$  ions  $\rightarrow \text{Ce (III)}$ ,  $\mu = 2.54 \text{ B.M.}$

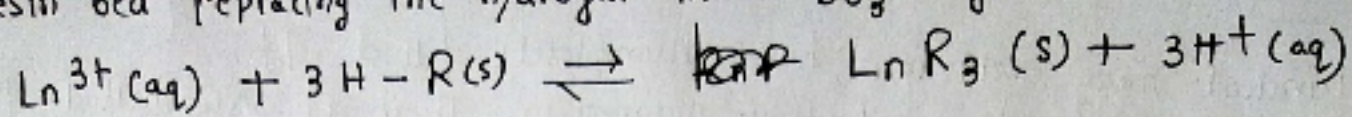
## Isolation of R.E.E by ion exchange method:

Size of the  $\text{Ln}^{3+}$  ion decreases gradually from  $\text{Ce}^{3+}$  to  $\text{Lu}^{3+}$  (lanthanide contraction). Accordingly, the binding of the  $\text{Ln}^{3+}$  ions to a complexing agent like EDTA gradually and regularly increases with increasing atomic number of R.E.E. So, when a mixture of  $\text{Ln}^{3+}$  ions bound on an ion exchange bed is eluted with a dilute soln. of EDTA under adjusted condition, R.E.E will be eluted in a sequence from higher atomic no. to lower atomic no. i.e.  $\text{Lu}^{3+}$  is eluted first.

A soln. containing various  $\text{Ln}^{3+}$  ions is run down a column of cation exchange resin when the  $\text{Ln}^{3+}$  ions are absorbed in the

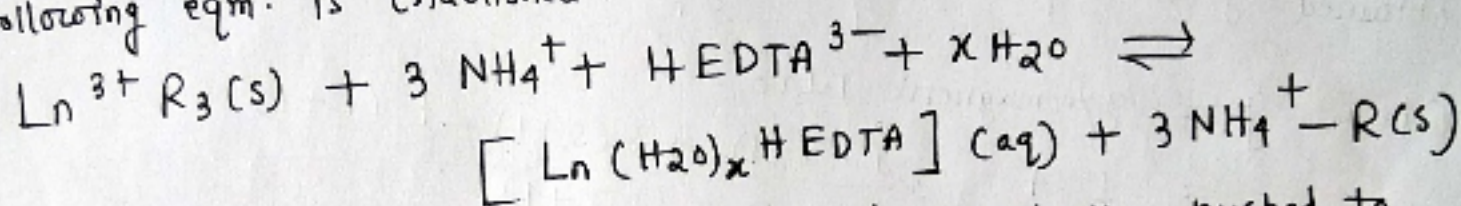


resin bed replacing the hydrogen in  $-SO_3H$  gr.



where  $[R = \text{Resin}]$

Affinity of the  $Ln^{3+}$  ions for the resin increases slightly with increase in atomic no. but this is not sufficient to effect a good separation. The  $Ln^{3+}$  ions are washed down or eluted from the resin bed with a proper complexing agent (dil. soln. of triammonium-EDTA) at  $pH \approx 8$  or a buffered soln. of citric acid/ammonium citrate. The following eqm. is established:



At any point in the column, the eqm. is gradually pushed to right with the continuous arrival of fresh eluting agent and removal of the  $Ln^{3+}$ -EDTA complex to the lower layers in the column. The process is in fact repeated automatically at various layers in the resin bed; as the heavier  $Ln^{3+}$  ions form stronger complexes with EDTA, they are gradually enriched in the soln. phase and are eluted in the reverse order of their atomic number. The different  $Ln^{3+}$  ions concentrate in bands in different regions in the column and their downward movement may be followed by atomic fluorescence spectroscopy.